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Optimization and Characterization of Synthesis Conditions of Adsorbent from Bone for Removal of Fluoride

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Abstract : ***This work aims to prepare adsorbents based on low cost cattle bones. The bones have sustained pyrolyzation in inert atmosphere at three different temperatures (400°C, 500°C and 600°C), time (60, 90 and 120 minutes) and inlet N_2 pressure (1.5, 2 and 2.5bar) in an electric furnace. The charcoals obtained were characterized by its percentage removal of fluoride ion from synthetic fluoride water and naturally fluoridated water. The effect of contact time, adsorbent dosage, pH, temperature in shaker and initial concentration of fluoride was investigated. The adsorption was rapid during the initial one hour. The adsorption efficiency of bone char for fluoride removal was increased with adsorbent dosage. The defluoridation capacity was appreciable at neutral pH.Bone waspyrolyzed in the range between 400 to 500°C and it gave better fluoride removal. The fluoride adsorption efficiency depends directly on initial fluoride concentration. The adsorption data were well fitted to the Freundlich isotherm model. The adsorption capacity and adsorption intensity at equilibrium(q_e) are 12.075mg/g and 1.548 respectively.***

***Keywords**: pyrolyzation,* potassium fluoride, UV-vis spectrophotometer

Introduction

Fluoride has both beneficial and harmful effects on the human health depending upon its level. Among the beneficial effects of fluoride in human body, strengthening of bones and prevention from tooth decay are significant [27]. Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis, and long-term damage to the brain, liver, thyroid and kidney [30]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity [29]. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite [31].

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4) F + OH^-$$

Fluoroapatite being more resistant to acid attack compared to hydroxyapatite offers a protective layer to the tooth enamel against acids from foods. This prevents dental caries. Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide [31].

$$Ca_5(PO_4)_3 F + 9F^- \rightarrow CaF_{10} + 3PO_4^{3-}$$

Adsorption is a mass transfer operation in which substances present in a liquid phase are adsorbed or accumulated on a solid phase and thus removed from the liquid [4].

Materials and methods

Equipments: The major equipments used are tubular furnace which can operate up to a temperature of 1200°C, UV-vis spectrophotometer (HACH DR3900), water bath heater, shaker, centrifuge, oven, sieve, mechanical size reduction (mill), analytical balance, beaker plastic bottles and pH meter.

Chemicals: The major chemicals used are bone waste, potassium fluoride (KF), hydrochloric acid, sodium hydroxide, distilled water, nitrogen gas which was used to ensure an inert atmosphere in the furnace and used as factor.

Methods

Experimental procedure

The raw material was collected from Burau which is located near to west of Addis Ababa. The raw material was crushed into smaller size using axe and flesh was removed by washing with hot water. The crushed bone was soaked in boiling water in order to degrease at 90°C. When the water became free from grease, the bone was placed in the oven at 105°C for one hour. Mass of 125g bone was measured for each run and introduced into the furnace. After collecting the product, the charcoal was further crushed into fine particle using grinding machine. Bone char was screened using sieve of 1mm size in order to obtain particles below 1mm. Fluoridated water was prepared using KF. Adsorption test results were analyzed for different char and conditions expected to affect adsorption.

Result and discussion

Effect of Parameters on Pyrolysis of Bone

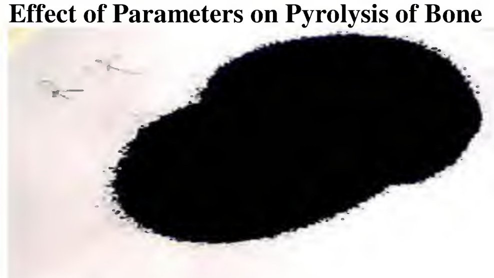

Figure1. Bone charcoal obtained at 500°C, 90min and 2.5bar.

Effect of Pyrolysis Temperature

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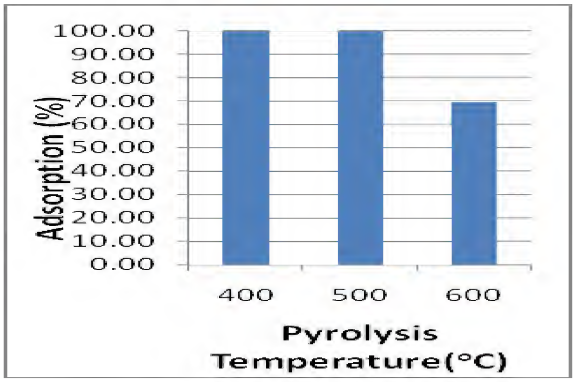
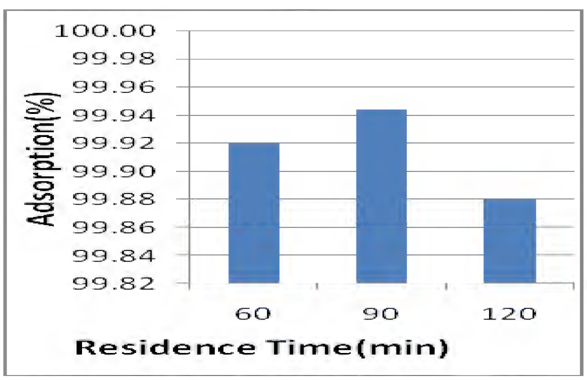
The maximum charcoal yield was obtained when the bone was pyrolyzed at a temperature of 400°C. In contrast, the yield gradually decreased as the pyrolysis temperature increased.

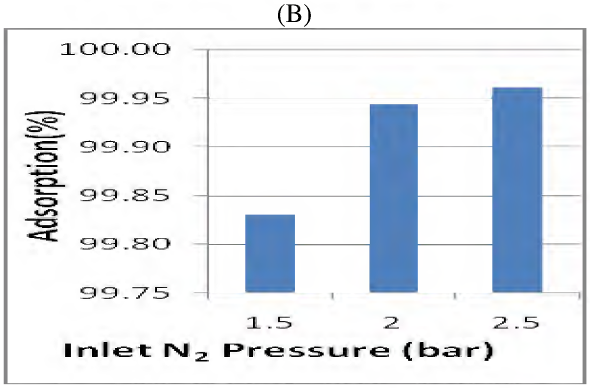
The effect of pyrolysis temperature on the removal efficiency of charcoal towards fluoride is shown in Figure2.A(at 2bar and 90min). The highest fluoride removal efficiency was observed for a charcoal prepared in range 400°C to 500°C and less removal efficiency was obtained for the adsorbent produced at 600°C. For temperatures up to 400°C, the bone char might be incompletely burned, thus resulting in less fluoride uptake by the bone char. Removal capacity at temperatures beyond 500°C (600 – 700°C) was again reduced.



(A)



(B)



(C)

Figure.2. The effect of pyrolysis temperature(A), residence time(B) and inlet N_2 pressure(C) on the adsorption capacity of bone char for fluoride ion from water.

Effect of Pyrolysis Time

The less amount of bone char was collected from 120 minute pyrolysis time which was 54.08% of the input.

Figure2.B(at 2bar and 500°C) shows that, as the pyrolysis time increased the percentage removal of fluoride slightly decreased. But, pyrolysis time of 90 minute results the best adsorbent than the rest if 500°C and 2bar is chosen. The reason for this is that as bone exposure to heat increase the calcium hydroxyapatite decomposition increase, making less ion exchange possible.

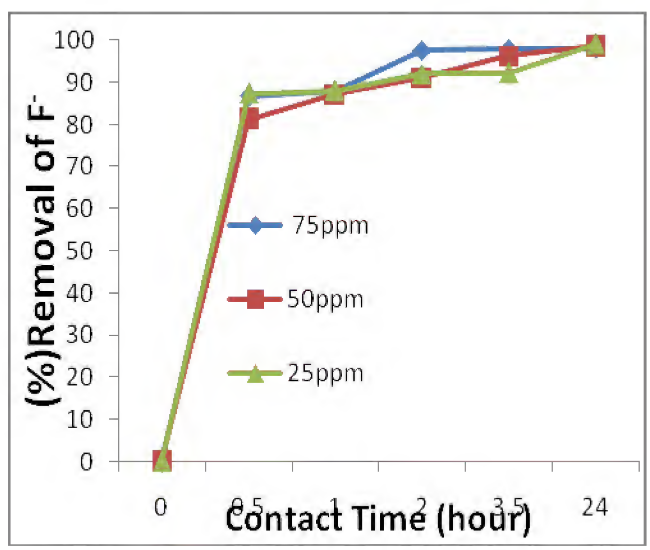
Effect of Inlet Nitrogen Pressure

Operating at high inlet nitrogen pressure reduce the product quantity. The maximum amount of product is obtained at the 1.5bar. The decrement on the product yield is due to the release of more volatile components at higher pressure beyond 1.5bar.

Figure2.C (at 90min and 500°C) shows the effect of inlet nitrogen pressureon the adsorption efficiency of bone char. The pyrolyzing the raw material at all inlet nitrogen pressure has no significant difference for adsorption of fluoride. The first purpose of using nitrogen is to create inert atmosphere in order to hinder side combustion reaction. The second purpose is to affect the surface of bone char in order to increase adsorption. The observed adsorption increment due to nitrogen was not significant.

The Effect of Contact Time

The effect of contact time on removal of Fluoride using bone char is presented graphically as percentage fluoride (F^-) removal at different contact times. Contact time was found to have an effect on the amount of fluoride removed per unit weight of bone char. It may be observed from the Figure3.A that as contact time increases, percent removal also increases initially and reduces gradually with time and attains almost an equilibrium condition and remains more or less constant thereafter.



(A)

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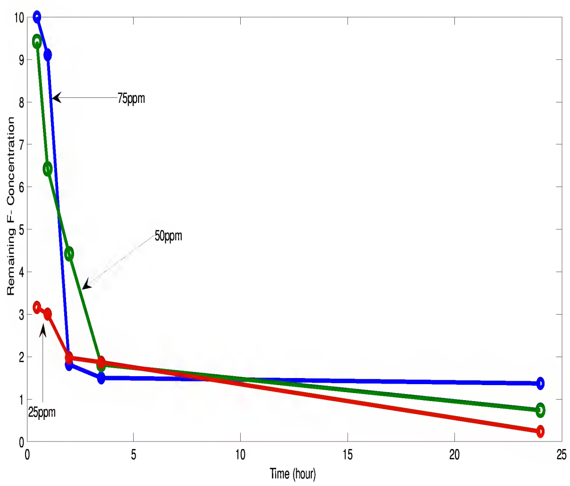


(B)

Figure 3. The effect of contact time (A) and initial fluoride concentration(B)on the fluoride removal efficiency.

The Effect of Initial Fluoride Concentration

Figure3.B shows that initial fluoride concentration influence on the removal capacity of the bone char, where the amount of fluoride adsorbed increased with increasing initial fluoride concentration from 4.4-14.728mg/g at initial concentration ranging from 25-75mg/l. This is attributable to the increased concentration gradient between the liquid and the solid phases which increasingly exceeds the mass transfer resistance between the solution and the bone char.

The Effect of Bone Char Dose

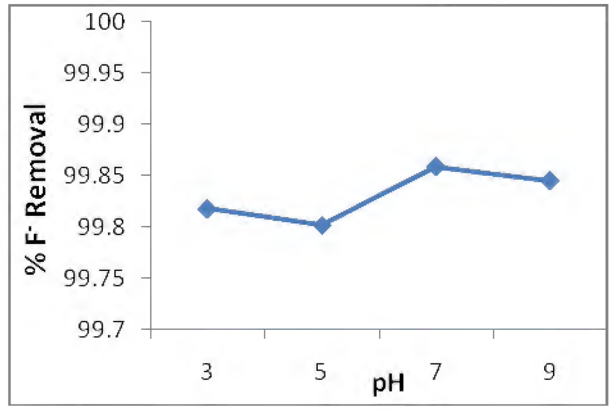
As shown in Table 4.2 the effect of bone char dose indicated that the removal capacity of fluoride increased with increased of the bone char dose.

Table1: Dose of bone char versus fluoride removal

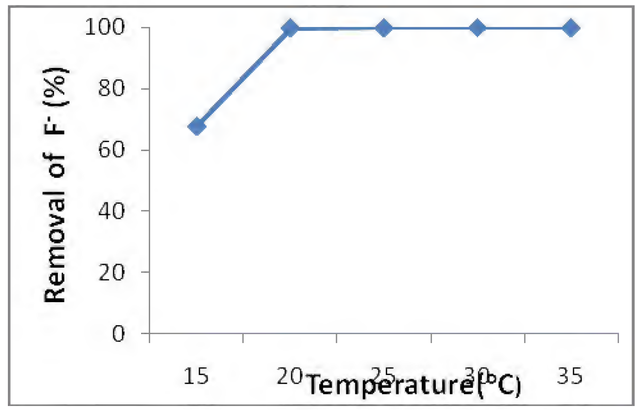
Dose (g/100ml)	0	1	2	3
Remaining F^- (mg/l)	4.25	1.28	1.25	1.20
Adsorption per unit mass of char (mg/g)	-	0.297	0.15	0.102

The Effect of pH

The pH at which bone char performs maximally is 7. According to this study the pH has no significant effect on the removal capacity of bone char. Figure4.A shows the results obtained at pH 3, 5, 7 and 9.



(A)



(B)

Figure.4. The effect of pH(A)and temperature(B) on fluoride removal of at 25^{o}C, 200rpm, 1g bone char, and 60min.

The Effect of Temperature within the Shaker on Adsorption Efficiency

The maximum fluoride removal was seen in the temperature range of 25^{o}C to 30^{o}C. The removal efficiency of bone char decreased for temperature lower than 20^{o}C.

Removal of Fluoride from Naturally Fluoridated Water by Bone Char

As an approximation of the results of the present work for application to a real problem, Fluoride containing water collected from National Tobacco Enterprise S.C farm area which is located near to Hawassa, southern Ethiopia. Two water samples were found to contain 4.25mgF^-/l and 4.725mgF/l. Taking the first water sample, adsorption capacity of bone char prepared under different conditions were investigated. All test results indicated in less than one mill grams of fluoride per litter (mgF^-/l) remaining after adsorption for contact time of 24 hours.

Optimum Pyrolysis Condition

The optimization of the production conditions of bone char adsorbent from bone was done by using response surface methodology (RSM). The effect of pyrolysis temperature, pyrolysis time and inlet N_2 pressure were investigated on the responses of yield and adsorption. Variance analysis (*ANOVA*) of the obtained quadratic model showed that the significant factors for adsorption and yield were temperature and time. The optimal conditions found from the RSM were temperature of 400 °C to 550°C, time of 60 to 90minutes and inlet N_2 pressure of 1.5bar, resulting in bone char with 99% fluoride removal, yield greater than 60%. Adsorption is our main response so that the optimum condition determined based on adsorption result found in the range 400 to 550°C for temperature, 60 to 90minutes for time and 1.5bar for inlet N_2 pressure. In order to avoid the unwanted color and taste due to organic components of the bone and at the same time to obtain greater adsorption for fluoride, it is better to prepare the bone char at condition that convert all organic matter into inorganic matter.

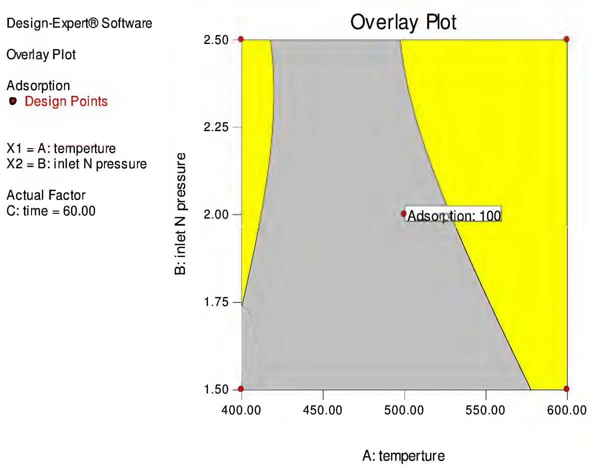


Figure.5. Optimum fluoride removal region

As shown in the Figure 5 the maximum adsorption obtained in the region shadded with gray color. Optimization by response surface methodology gave 100% adsorption in the gray region. All factors namely temperature, time and nitrogen minimized at lower left part of gray region. But in order to hinder the effect of color and taste it is better to choose optimum point at 500°C, 60 minutes and 1.5bar.

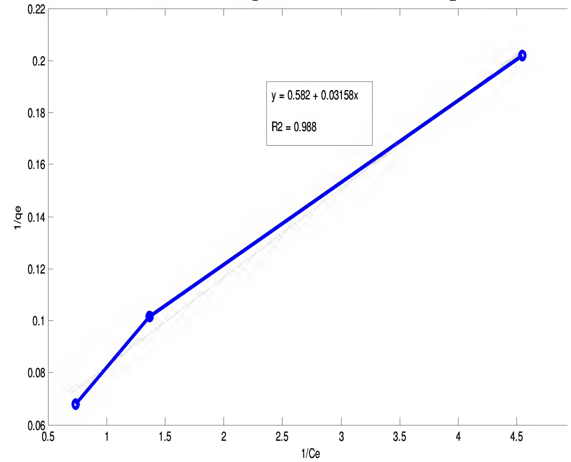
Adsorption Isotherm Models

Langmuir isotherm model

The constants in the Langmuir isotherm can be determined by plotting (1/qe) versus (1/ Ce) and making use of Langmuir equation rewritten as:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKl}(1/C_e) \ldots\ldots\ldots\ldots\ldots 1$$

Where q_m and K_l are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of q_m and K_l were determined from the Figure 6 ($1/C_e$ Vs $1/q_e$).



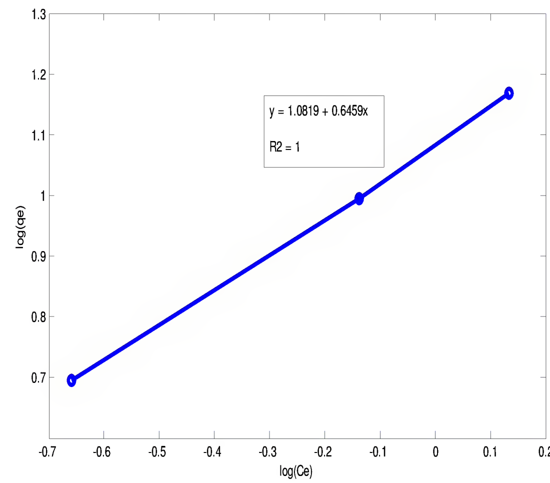


Figure.6. Langmuir isotherm model curve Figure.7. Freundlich Isotherm modelcurve

Freundlich Isotherm Model

Freundlich adsorption isotherm is the relationship between the amounts of fluoride adsorbed per unit mass of adsorbent, q_e, and the concentration of fluoride at equilibrium, C_e is related to qe as shown below.

$$q_e = K_f C_e^{1/n} \ldots\ldots\ldots\ldots\ldots 2$$

The logarithmic form of the equation becomes

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \ldots\ldots\ldots\ldots 4.3$$

Figure 7 shows, the plot of $\log(C_e)$ Vs $\log(q_e)$, was employed to generate the intercept value of $\log K_f$ and the slope of 1/n.

Table2: Adsorption isotherm model parameters

Freundlich Model	Langmuir Model
K_f =12.0752	q_m =34.388
N =1.5483	K_l=1.8157
R^2 =1	R^2 =0.988

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Therefore, Freundlich model is selected to be the best model for describing the adsorption of fluoride by the bone char. The adsorption capacity and adsorption intensity for the Freundlich model at equilibrium (q_e) are 12.075mg/g and 1.548 respectively.

Adsorption Kinetics Models

Pseudo first order kinetics model

$\log(q_e - q_t) = \log(q_e) - \frac{K1}{2.303}t$.....................4

As shown in Figure 8.A the values of log (qe – qt) were linearly correlated with t. The plot of log (qe – qt) versus t should give a linear relationship from which k_1 and qe can be determined from the slop and intercept of the plot, respectively.

Pseudo second order kinetics

The pseudo second-order adsorption kinetic rate equation is expressed as:

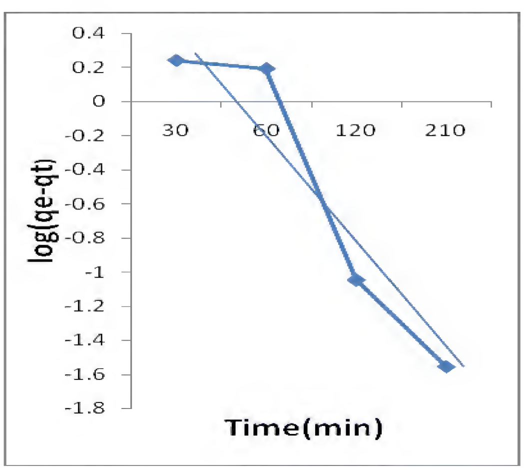
$\frac{dqt}{dt} = K_2(q_e - q_t)^2$ 5

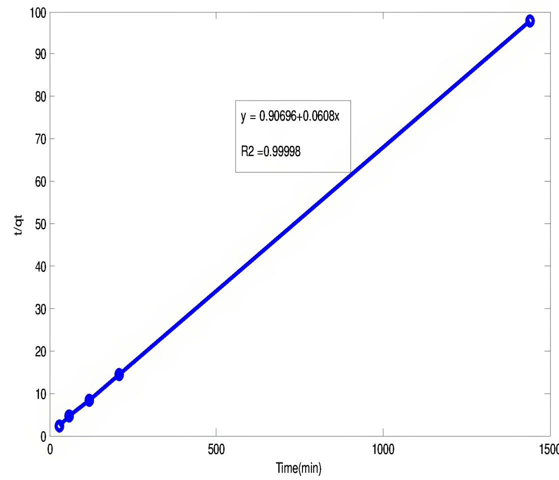
Where: k_2 is the rate constant of the pseudo second order adsorption (g/mg.min). For the boundary conditions t=0 to t=t and q_t=0 to q_t=q_e, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}(t)$.................................6

Where $h=K_2(q_e)^2$

The plot of (t/q_t) and t should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. From the Figure8.B, the best kinetic model that fits to the adsorption process is obtained to be pseudo second order kinetics model. Therefore, this model is selected to be the best model for the bone char used. Hence, taking pseudo second order as best kinetics model, the parameters such as equilibrium mass of adsorption is found to be 14.733mg/g for the 75ppm and its rate of adsorption (k_a) values are found to be 2.151g/(mg·min) respectively.





A B

Figure 8. Pseudo first(A) and pseudo second(B) order kinetics curve for 75ppm

Thermodynamic Studies

Change in Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o), were evaluated using the following Equations [49]:

$\ln(K_d) = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} = -\frac{\Delta G^o}{RT}$................................7

Where K_d is the equilibrium partition constant calculated as the ratio between adsorption capacity (q_e) and equilibrium concentration (C_e), R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin (K). The values of ΔH^o and ΔS^o obtained from the plot of $\ln(K_d)$ vs. 1/T. The plot of $\ln(k_d)$ as a function of 1/T should give a linear relationship with slope of $\Delta H°/R$ and an intercept of $\Delta S°/R$. Then $\Delta G°$ is obtained at any temperature from the following equation (4.8).

$\Delta G° = -RT \ln(K_d)$...............................8

Table 4.8 Thermodynamic parameters for adsorption of fluoride onto bone char

T(K)	ΔG^o(KJ/mole)	ΔS^o(J/(mole.K))	ΔH^o(KJ/mole)
293	-9.57	115.4	24.11
298	-9.96		
303	-10.86		
308	-10.27		

Conclusion

From the results of this work, it is concluded that bone can be used as raw material for the production of bone char adsorbent for fluoride removal. One of the novelties of this work is the optimization of the process parameters namely, temperature,

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residence time and nitrogen gas pressure during charcoal preparation.

Therefore, bone char can be used efficiently and effectively for fluoride removal from drinking water and waste water with appropriate selection of synthesis conditions for bone char preparation processes. According to this study it is concluded that optimum conditions were 500°C, 60 minutes and 1.5bar nitrogen.

References

i. Carbtrol ® Corporation, (1992). Granular Activated Carbon for Water & Wastewater Treatment.

ii. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, (2012). A Citizen's Guide to Activated Carbon Treatment.

iii. www.epa.gov/superfund/sites

iv. www.cluin.org

v. FerhanCecen and OzgurAktas, (2011).Water and Wastewater Treatment: Historical Perspective of Activated Carbon Adsorption and its Integration with Biological Processes WILEY-VCH Verla g GmbH & Co. KGaA, Weinheim.

vi. John C. Crittenden, R. Rhodes Trussell, David W. Hand, Kerry J. Howe and George Tchobanoglous, (2005). Water Treatment: Principles and Design, Second Edition, Published by John Wiley & Sons, Inc., Hoboken, New Jersey

vii. Juan Carlos Moreno, Rigoberto Gómez and LilianaGiraldo, (2010). Removal of Mn, Fe, Ni and Cu Ions from Wastewater Using Cow Bone Charcoal. www.mdpi.com/journal/materials

viii. N. SlimaniAlaoui, A. El Laghdach, E. Manuel Cuerda Correa, M. Stitou, F. El Yousfi , N. Jbari,(2014). Preparation of Bone Chars by Calcination in Traditional Furnace, J. Mater. Environ.Sci.5(2).

ix. Juan C. Moreno-Piraján, LilianaGiraldo, Vanessa S. García-Cuello, (2011). Study of the Textural Properties of Bovine Bones Char under Different Conditions, Journal of Water Resource and Protection.

x. www.scirp.org/journal/jwarp

xi. M. E. Kaseva, (2006). Optimization of Regenerated Bone Char for Fluoride Removal in Drinking Water: a Case Study in Tanzania, © IWA Publishing 2006 Journal of Water and Health.

xii. Cooperative Extension Service Michigan State University, (1990). Home Water Treatment Using Activated Carbon, (new) Extension Bulletin wq23.

xiii. Muhammad Farhan, Abdul Wahid, AminaKanwal and J.N.B. Bell, (2013). Synthesis of Activated Carbon from Tree Sawdust and its Usage for Diminution of Color and Cod of Paper-mill Effluents.

xiv. British geological survey, (2001). Ground Water Quality: Ethiopia, NERC, Water Aid.

xv. Alexandra C. Huber, Robert Tobias, and Hans-Joachim Mosler, (2014). Evidence-Based Tailoring of Behavior-Change Campaigns: Increasing Fluoride-Free Water Consumption in Rural Ethiopia with Persuasion, applied psychology: health and well-being.